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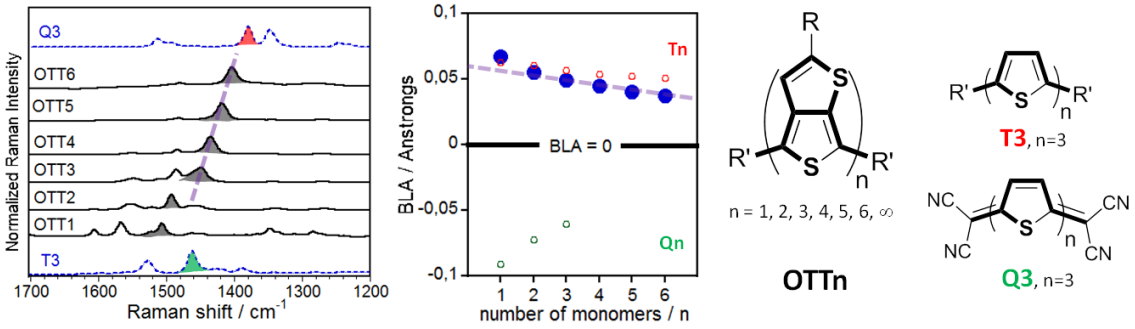
Abstract Title:

Thieno[3,4-b]thiophene Oligomers and Polymers: Low-Band Gap Molecules Based on a Large Quinoidization and Synergistic Aromaticity Competition.

Abstract text (500 words maximum)
The thieno[3,4-b]thiophene monomer has been conceived as the building block for the preparation of thieno[3,4-b] oligothiophenes (**OTTn**) from a dimer to a hexamer together with their corresponding polymers (1). These molecular designs are unprecedented in the important family of oligothiophenes. We have solved the synthetic problem related with the isomerization of the outer [3,4-b]thiophene regarding the central thiophene and obtained regioregular isomerically pure compounds.



The wavelengths of the band maxima of the low-energy lying electronic absorptions show a concomitant red-shift from the monomer to the hexamer without *saturation length* for the hexamer: for OTT6, λ_{max} = 720 nm which is a optical band gap of 1.7 eV, the lowest known for this class of homogeneous thiophene-based compounds. The same chain length effect is found in the Raman spectra. We ascribe this un-ended wavelength and frequency red-shift and bang gap contraction to the progressive quinoidization of the oligothiophene structure which is accompanied by a progressive reduction of the bond-length alternation pattern. An additional red-shift is observed passing to the chemically synthesized polymers based on the thieno[3,4-b]thiophene unit. We interpret these findings on the basis on the competition between the constant aromaticity of the outer [3,4-b]thiophene regarding the variable aromaticity of the linearly conjugating thiophenes. Because the subtle tuning of the aromatic competition

between the two units is proportional to the chain length, a progressive and proportional increment of quinoidization is observed in accordance with the no chain length saturation behavior. A complete characterization of the molecular properties of these new thieno[3,4-b] oligothiophenes and polythiophenes is provided by using Raman spectroscopy in conjunction with optical absorption and emission spectroscopies, time resolved fluorescence, and electrochemistry. Characterization of the OTTn oxidized species brings us another unprecedented result consisting on the complete inversion of the position and trend of the optical band wavelengths and optical gaps of radical cations versus dications and of the these regarding those of conventional oligothiophenes (Qn and Tn). Thieno[3,4-b] oligothiophenes represent a new family of organic π–conjugated substrates with promising application in organic electronics (2) as we will show in this communication.

References:

(1) Xiaozhang Zhu, Juan Casado, et al. manuscript in preparation.
(2) C. Zhang, Y. Zang, E. Gann, C. R. McNeill, X. Zhu, C. Di, D. Zhu, *J. Am. Chem. Soc.*, **2014**, *136*, 16176.

Presentation type – **invited oral**

Research category: **Design and synthesis of new π-conjugated molecules and polymers**